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THEORY OF GROUND- AND EXCITED STATE-PROPERTIES OF SOLIDS, SURFACES, AND
 INTERFACES: BEYOND DENSITY FUNCTIONAL FORMALISM

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ABSTRACT

Two recently developed approaches for calculating properties of materials going beyond the density functional formalism are discussed. For excited-state properties, a first-principles quasiparticle theory has been developed. The electron self-energy operator is calculated using the full dielectric matrix and the dressed Green's function. Electron excitation spectra are interpreted as transitions between quasiparticle states of an interacting many-electron system. For ground-state properties, a new method using nonlocal pseudopotentials in conjunction with the variational quantum Monte Carlo approach is introduced. Electron correlations are treated using the exact interaction with a correlated wavefunction of the Jastrow-Slater form. Selected examples from bulk, surface, and interface calculations are presented to illustrate the capabilities of these two approaches.

I. INTRODUCTION

A number of methods, going beyond pair-potentials, now exist for calculation of the structural and electronic properties of materials. These range from the use of classical many-body atomic potentials to semiempirical quantum approaches to parameter-free ab initio methods.¹ Among the first-principles methods, basically one of the following two approaches is employed in treating many-electron correlations: (1) the Hartree-Fock plus correlation corrections approach or (2) the local density functional formalism (LDA). The LDA is by far the more commonly employed approach. The Hartree-Fock-plus-corrections calculations have been mostly restricted to the lighter elements and to binding energies.

The LDA² has been applied to a wide range of materials with many successes.^{3,4} Among them are some striking results on the structural properties, vibrational properties, electron-phonon and phonon-phonon interaction parameters, and structural phase transitions. There are, however, problems with the LDA. The binding energies are significantly too large for virtually all molecular and solid-state systems. The ground-state properties of many magnetic and other highly correlated electron systems are not well described. Finally, since the density functional formalism is a ground-state theory, the eigenvalues from the LDA do not give accurate band gaps or in general electron excitation energies.⁵

In this paper, we give a short review of two recent theoretical developments in first-principles calculation of the ground- and excited-state properties of real materials. The calculated results are shown to be in significantly better agreement with experiment than those from state-of-the-art LDA or Hartree-Fock methods. The paper is organized as follows. In Sec. II, a quasiparticle approach⁶ for excitation energies in solids is discussed. Results for bulk solids as well as for semiconductor surfaces and heterojunctions are presented to illustrate the general applicability of the method. In Sec. III, an approach⁷ which combines the use of variational quantum Monte Carlo techniques with nonlocal pseudopotentials for ground-state properties is presented. Results from calculations on diamond and graphite are discussed. Finally, in Sec. IV we present a summary and some conclusions.

II. QUASIPARTICLES AND EXCITED-STATE PROPERTIES

It is well known now that, since the density functional formalism² is a ground-state theory, LDA calculations do not provide in principle direct information on the excitation spectra of an electronic system. Indeed, in most cases, the practice of comparing LDA eigenvalues to spectroscopic data has led to rather severe discrepancies.⁴ For example, the band gaps of semiconductors and insulators are drastically underestimated in the LDA by as much as 50% or more (see Table I). The optical and photoemission spectra of both bulk and surface states are similarly not well-described. The same problem exists even for the band gaps and widths of the simple metals such as sodium.⁸ The reason for these discrepancies is that the interpretation of excitation spectra such as those measured in optical, photoemission or transport experiments requires the concept of quasiparticles, the particle-like excitations in an interacting many-body system.^{5,9}

Recently, several many-body approaches have been proposed for calculating (either semi-empirically or from first-principles) the quasiparticle properties of solids going beyond the one-particle picture.^{6,10-14} For the special case of the minimum gap in insulators, an explicit correction to the Kohn-Sham minimum gap has also been derived and calculated.¹⁴ For a complete description of the excitation spectrum, direct quasiparticle calculations are however necessary. First-principles methods are of special importance for predicting the properties of new materials and those of defects or surfaces and interfaces.

In this section, we present a brief review of a first-principles quasiparticle approach⁶ which has shown to give highly accurate excited-state properties for real materials with basically the atomic number of the constituent elements as the only input. The method is based on the so-

Table I. Comparison of calculated band gap E_g (in eV) with experiment. The results for Ge include relativistic effects.

	LDA	Present Theory	Experiment
Diamond	3.9	5.6	5.48 ^a
Silicon	0.52	1.29	1.17 ^a
Germanium	<0	0.75	0.744 ^a
LiCl ₂	6.0	9.1	9.4 ^b

^aRef. 21

^bRef. 22

called GW approximation¹⁵ in which the electron self-energy operator is calculated to first order in the dressed Green's function G and the screened Coulomb interaction W .

A. The Self-Energy Approach

In the present approach, the quasiparticle energies are given by^{6,9}

$$(T + V_{\text{ext}} + V_H)\psi_{\vec{n}\vec{k}}(\vec{r}) + \int d\vec{r}' \Sigma(\vec{r}, \vec{r}'; E_{\vec{n}\vec{k}}) \psi_{\vec{n}\vec{k}}(\vec{r}') = E_{\vec{n}\vec{k}} \psi_{\vec{n}\vec{k}}(\vec{r}) \quad (1)$$

where T is the kinetic energy operator, V_{ext} is the external potential due to the ions, V_H is the average (Hartree) Coulomb potential, and the exchange and correlation contributions are included in the self-energy operator, Σ . In general, Σ is nonlocal, energy-dependent, and nonHermitian with the imaginary part giving the lifetime of the quasiparticles.

The self-energy operator Σ can be systematically expanded in a series in terms of the screened Coulomb interaction W and the fully dressed Green's function G .¹⁵ In the GW approximation, Σ is taken to be the first-order term with

$$\Sigma(\vec{r}, \vec{r}'; E) = i \int (d\omega/2\pi) e^{-i\delta\omega} G(\vec{r}, \vec{r}'; E - \omega) W(\vec{r}, \vec{r}'; \omega), \quad (2)$$

where δ is a positive infinitesimal. The major components of the theory are then the fully interacting Green's function for which we use a quasiparticle approximation

$$G(\vec{r}, \vec{r}'; E) = \sum_{\vec{n}\vec{k}} \frac{\psi_{\vec{n}\vec{k}}(\vec{r}) \psi_{\vec{n}\vec{k}}^*(\vec{r}')}{E - E_{\vec{n}\vec{k}} - i\delta} \quad (3)$$

and the dynamically screened Coulomb interaction

$$W(\vec{r}, \vec{r}'; \omega) = \Omega^{-1} \int d\vec{r}'' \epsilon^{-1}(\vec{r}, \vec{r}''; \omega) V_C(\vec{r}'' - \vec{r}'), \quad (4)$$

where ϵ is the time-ordered dielectric matrix whose off-diagonal elements in Fourier space describe the local fields (variation in the screening in the unit cell due to charge inhomogeneity) and V_C is the bare Coulomb interaction. Our approach⁶ is to take Eq. (2) as the basic approximation and proceed to calculate Σ from first principles with minimum further approximations.

The quasiparticle energies together with Σ and G must be obtained in a self-consistent fashion. In the calculations, the electron Green's function is constructed initially using the LDA Kohn-Sham eigenfunctions and eigenvalues and is subsequently updated with the quasiparticle spectrum from Eq. (1). The static dielectric matrix $\epsilon(\vec{r}, \vec{r}'; \omega = 0)$ is obtained as a ground-state quantity from the LDA calculation and extended to finite frequencies using a generalized plasmon pole model with exact sum rules.^{6,16}

This approach has been applied successfully to a variety of solids including semiconductors,⁶ ionic insulators,¹⁷ and metals¹⁸ as well as surfaces¹⁹ and interfaces.²⁰ For a full physical description of the quasiparticles, it is found that the use of the crystalline Green's function and inclusion of both local fields (the full dielectric matrix) and dynamical screening effects are important factors. For semiconductors and insulators, local field effects are of crucial importance. For the alkali metals, the quasiparticle bandwidths are shown to be also sensitive to the treatment of exchange-correlation effects in the dielectric screening.¹⁸

B. Band Gaps and Excitation Spectra of Crystals

Very accurate band gaps, optical transition energies, and photoemission spectra have been obtained using the quasiparticle approach.^{6,17,18} For the case of the minimum gap, this is illustrated in Table I where the calculated results for several selected crystals are compared to the experimental values. As seen from the table, the gaps open up dramatically as compared to the LDA eigenvalues. Similar results have been obtained for the ionic semiconductors, e.g. GaAs and AlAs.^{20,23} This level of accuracy is achieved only when both local fields and dynamical screening effects are included in the evaluation of the electron self-energy operator.

For the optical properties of semiconductors, the agreement between theory and experiment is generally at the same level as for the minimum gaps. A comparison between experimental direct optical transitions^{21,24-27} and calculated results are given in Table II for diamond, Si and Ge. The theoretical results are within 0.1-0.2 eV of the experimental values for all transitions except for the very high energy ones in diamond where the experimental uncertainties are large. This excellent agreement is a dramatic improvement over previous theories.¹⁰⁻¹³ In fact, the present quasiparticle results are comparable to results from the Empirical Pseudopotential Method²⁸ in which the band structure is obtained by fitting to optical data using several parameters.

In addition to the minimum band gaps and optical transition energies, the theory yields excellent band dispersions. Figure 1 depicts the calculated Ge quasiparticle valence band structure together with data from angle-resolved photoemission measurements.²⁹ The agreement between theory and experiment is generally within experimental errors. Similar levels of agreement with experiment have been obtained for other semiconductors and for empty band states as measured in inverse photoemission experiments.⁶ A comparison of the calculated band structure with photoemission data for Na³⁰ is given in Fig. 2. The surprisingly large observed bandwidth reduction is

Table II. Comparison between theory and experiment for optical transitions in Ge, Si, and diamond

	LDA	Present Work	Experiment
<u>Ge</u>			
$\Gamma_{7v} \rightarrow \Gamma_{8v}$	0.30	0.30	0.297 ^a
$\Gamma_{8v} \rightarrow \Gamma_{7c}$	-0.07	0.71	0.887 ^a
$\Gamma_{8v} \rightarrow \Gamma_{6c}$	2.34	3.04	3.006 ^a
$\Gamma_{8v} \rightarrow \Gamma_{8c}$	2.56	3.26	3.206 ^a
$X_{5v} \rightarrow X_{5c}$	3.76	4.45	4.501 ^a
<u>Si</u>			
$\Gamma_{25'v} \rightarrow \Gamma_{15c}$	2.57	3.35	3.4 ^b
$\Gamma_{25'v} \rightarrow \Gamma_{2'c}$	3.26	4.08	4.2 ^c
$L_{3'v} \rightarrow L_{1c}$	2.72	3.54	3.45 ^b
$L_{3'v} \rightarrow L_{3c}$	4.58	5.51	5.50 ^b
<u>Diamond</u>			
$\Gamma_{25'v} \rightarrow \Gamma_{15c}$	5.5	7.5	7.3 ^d
$\Gamma_{25'v} \rightarrow \Gamma_{2'c}$	13.1	14.8	15.3 \pm .5 ^e
$X_{4v} \rightarrow X_{1c}$	10.8	12.9	12.5 ^c

^aRef. 24 ^bRef. 25 ^cRef. 21 ^dRef. 26 ^eRef. 27

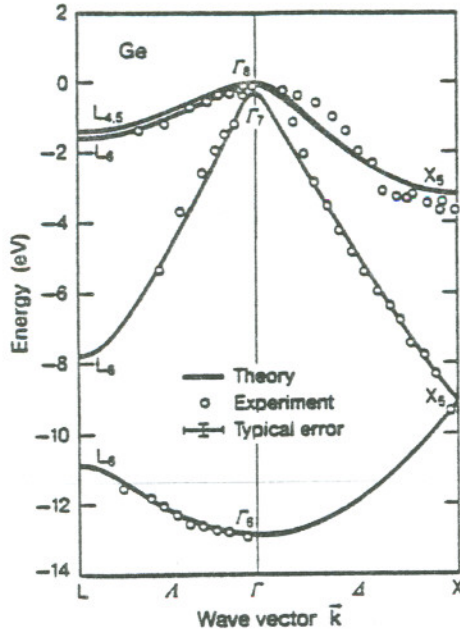


Fig. 1. Photoemission data from Ref. 29 vs. theoretical quasiparticle energies.

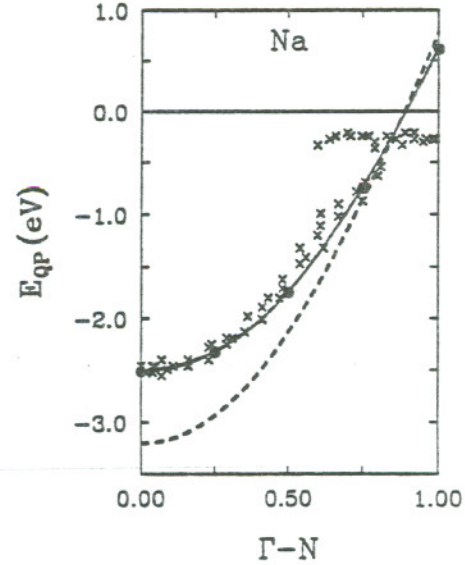


Fig. 2. Quasiparticle energies for Na: Experimental data from Ref. 30 (crosses), LDA eigenvalues (dashed line), and calculated quasiparticle energies (filled circles).

explained by the self-energy effects although the origin of the dispersionless feature near the Fermi energy remains a subject of debate.

Another important result from the calculations is that the quasiparticle wavefunctions are found to be remarkably well represented by the LDA wavefunction. For the materials considered, the quasiparticle wavefunction, in general, has better than 99.95% overlap with the corresponding LDA wavefunction although the energy spectrum is altered significantly as seen in Table I. The approximation of using only the diagonal element $\langle nk | \Sigma | nk \rangle$ in evaluating the quasiparticle energies leads to errors ranging from less than 0.01 eV for Si to less than 0.05 eV for LiCl. This approximation thus may be used with only negligible loss of accuracy in the final quasiparticle energies.

C. Surface and Interfaces

The quasiparticle theory has been extended to surfaces and interfaces. We discuss here results for two prototypical systems -- the As-capped Si(111) and Ge(111) surfaces¹⁹ and the GaAs-AlAs(001) heterojunction.²⁰ The major objective is to provide a predictive theory for surface-state energies and band offsets at interfaces.

At saturation coverage, the chemisorbed As atoms are found to substitute for the outermost-layer atoms on the Si(111) and Ge(111) surface.³¹⁻³³ The surface becomes chemically inactive and is stable against reconstruction showing a 1×1 periodicity. These are good prototype systems for the many-body calculations because of their geometric simplicity and the availability of detailed experimental data.³¹⁻³³ They are also of intrinsic importance as an initial stage of growth of GaAs on Si and Ge. The calculations¹⁹ were carried out using a repeated slab geometry with a 12-layer thick slab. The surface geometry was determined by a LDA total energy minimization. After the structure has been determined, the quasiparticle energies for both the

bulk and surface states are then calculated using the same formalism as in the case of bulk crystals.

Figure 3 depicts the calculated quasiparticle energies for the As-capped Si(111) system. The quasiparticle surface-state bands (solid lines) together with the LDA surface-state bands (dashed lines) are plotted against the projected quasiparticle band structure of Si. The zero of the energy scale is set at the valence band maximum. As expected, the fully occupied surface band corresponds to the lone-pair states of the As adatoms. These surface states have been studied in detail using angle-resolved photoemission techniques.³¹ The theory also predicted an empty surface state band in the gap. These empty states correspond to backbond surface states. Very similar results are obtained for the Ge(111)-As surface.

For both the Si(111)-As and Ge(111)-As surface, the occupied quasiparticle surface-state band is lower in energy and has a broader dispersion as compared to the LDA results. These changes bring the theoretical energies into close agreement with experiment. Figures 4 and 5 compare the quasiparticle surface-state band with angle-resolved photoemission data. The agreement is excellent in both the placement and the width of the band and is well within the estimated errors of ± 0.1 eV with experiment and theory. As seen in Fig. 3, the effect of many-body correction to the LDA values on the empty surface states is even more dramatic. These states are substantially shifted upwards in energy, opening up the gap between empty and occupied surface states by nearly an extra 1 eV at some k-points. A scanning tunneling microscopy study³⁴ has recently been done for the Si(111)-As surface to search for these states. Not only is the 1×1 surface structure seen directly, the observed surface-state gap of 1.9 - 2.3 eV in the normalized differential conductivity agrees very well with the predicted value of 2.2 eV.

The surface quasiparticle results, therefore, address the difficulties associated with the LDA surface-state energies in ways very similar to the bulk excitation energies. In particular, the gap between the empty and filled surface states is substantially opened in comparison with the LDA surface-state gap. Analysis of the calculated results,¹⁹ however, shows that the size of the correction depends on the detailed character of the surface states which can have a substantially different character than the bulk states. This means that the shortcomings of the LDA surface-state spectra cannot easily be corrected by a simple rigid shift derived from bulk data.

Using the same theoretical techniques, we have computed the band offsets of the GaAs-AlAs(001) interface.²⁰ The band discontinuities at a semiconductor interface are simply the differences in the quasiparticle energy E_{qp} across the junction for the band edge states. Since, as mentioned above, the quasiparticle wavefunctions are virtually identical to the LDA wavefunctions, we may write E_{qp} near an interface as

$$E_{\vec{n}\vec{k}}^{qp} = \epsilon_{\vec{n}\vec{k}}^{LDA} + \Sigma_{\vec{n}\vec{k}} - V_{xc}^{\vec{n}\vec{k}} \quad (5)$$

where $\Sigma_{\vec{n}\vec{k}}$ and $V_{xc}^{\vec{n}\vec{k}}$ are, respectively, the expectation value of the self-energy operator and the LDA exchange-correlation potential for a given state. Then, the valence band offset ΔE_v becomes

$$\Delta E_v = \Delta E_v^{LDA} + \delta_{vbm} \quad (6)$$

where ΔE_v^{LDA} is the LDA calculated valence band offset and δ_{vbm} is a many-body correction given by

$$\delta_{\text{vbm}} = (\Sigma - V_{\text{xc}})_{\text{GaAs}}^{\text{vbm}} - (\Sigma - V_{\text{xc}})_{\text{AlAs}}^{\text{vbm}} . \quad (7)$$

Since the quasiparticle energies in determining the band offsets should be evaluated at a distance away from the interface and both Σ and V_{xc} are short range interactions, $(\Sigma - V_{\text{xc}})^{\text{vbm}}$ can be replaced by their bulk values. To calculate the LDA band offsets, we perform a 12-layer superlattice calculation using an approach similar to that of Van de Walle and Martin.³⁶

We find that the many-body correction to the valence band offset is quite significant; that is, $\delta_{\text{vbm}} = 0.12$ eV. It is about 30% of the LDA result of $\Delta E_{\text{v}}^{\text{LDA}} = 0.41$ eV. Equation (6) thus gives a calculated value of $\Delta E_{\text{v}} = 0.53$ eV which is in good agreement with recent experimental values of 0.53 - 0.56 eV.³⁷ The sign of the many-body correction can also be understood in terms of a more localized valence band wavefunction for AlAs which leads to a more negative self-energy for the valence band states of AlAs as compared to GaAs, and, hence, a positive value for δ_{vbm} as defined by Eq. (7). We expect that similar corrections will be even more important for junctions that are made of materials with lesser chemical similarities than GaAs and AlAs.

III. QUANTUM MONTE CARLO CALCULATION OF GROUND-STATE PROPERTIES

In this section we describe a method⁷ of performing variational quantum Monte Carlo calculations for solids and atoms using nonlocal pseudopotentials. The goal is to provide a first principles method which would be capable of treating accurately the properties of some of the strongly correlated electronic systems.

A. Variational Quantum Monte Carlo Method with Nonlocal Pseudopotentials

The variational quantum Monte Carlo (QMC) method was pioneered by McMillan³⁸ to study liquid He⁴ and first applied to fermion liquid problems by Ceperley, Chester, and Kalos.³⁹ However, a straightforward application of the method to the electronic properties of real materials has been severely hampered by a number of conceptual and technical problems. Among these include the treatment of the single-particle orbitals in the presence of electron correlations and the very rapid growth of computation effort with increasing atomic number caused by fluctuations in the energies of electrons in the core region.⁴⁰ This has prompted our development of a quantum Monte Carlo pseudopotential approach, which incorporates the effects of the core electrons in an ionic potential. The ionic pseudopotentials used are the norm-conserving pseudopotentials.⁴¹ The integral operator which arises in the nonlocal pseudopotential makes the present problem different from previously considered QMC problems. However, this operator can be evaluated statistically within the variational QMC method with a computational effort comparable to that for the kinetic energy.^{7,42}

In the present approach, a correlated trial wavefunction of the Jastrow-Slater form,

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \exp \left\{ \sum_{i=1}^N x(\vec{r}_i) - \sum_{1 \leq i < j \leq N} u(\vec{r}_{ij}) \right\} D(\vec{r}_1, \dots, \vec{r}_N) , \quad (8)$$

is employed where D is a Slater determinant of LDA single-particle wavefunctions. For this wavefunction we evaluate the expectation value of the exact many-electron Hamiltonian

$$H = \sum_{i=1}^N \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}}(\vec{r}_i) + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{r_{ij}} \right\}, \quad (9)$$

which consists of the usual three terms: the kinetic energy of the valence electrons, an external potential due to the ions, and the Coulomb interactions between the electrons. The many-body integrals are evaluated using the Metropolis Monte Carlo algorithm⁴³ for importance sampling with the importance function $|\psi|^2$. In the calculation, the kinetic and electron-electron energies are evaluated as in Ref. 39. The external potential is the sum of the ionic pseudopotentials which have a local and a (short-range) nonlocal part. The value of the local potential at each configuration of the random walk is evaluated using Ewald summation techniques. The value of the nonlocal potential is evaluated using a statistical method with a special point scheme.^{7,42}

The two-particle correlation term, $u(\vec{r}_{ij})$, in the Jastrow factor lowers the energy by reducing the probability of two electrons coming close together. In the solid, this term is taken to be of the standard form,³⁹ $u(r) = A[1 - \exp(-r/F)]/r$, with A and F as spin-dependent variational parameters. For diamond and graphite, the optimum values for A and F are found to be very close to the values given by the physical considerations of the so-called "tail" and "cusp" conditions.³⁹ In the atom, we have used both the form of $u(r)$ for the solid and $u(r) = -ar/(1 + br)$ and obtained essentially identical total energies.

The one-particle term $\chi(\vec{r})$ allows a variational adjustment of the single-particle orbitals in the presence of the two-particle term which tends to make the charge density overly diffuse. Although not relevant in liquids, the one-particle term is quite important for atoms and solids. There are several possible implementations of the one-particle term including the use of an Euler-Lagrange equation for χ to minimize the energy.⁴² In the calculation discussed here, we simply set $\chi(\vec{r}) = \alpha \log[\rho_{\chi, u=0}(\vec{r})/\rho_{\chi=0}(\vec{r})]/2$, where $\rho(\vec{r})$ is the charge density and α is a variational parameter. The optimum value of α is close to 1, as expected, since the LDA charge density is generally quite good.

B. Application to Atomic Carbon, Diamond, and Graphite

The ionization energy and electron affinity of atomic carbon are obtained by performing calculations on $C(3P)$, $C^+(1P)$, and $C^-(4P)$. In each case, we fixed the parameter a in $u(r)$ using the cusp condition and searched the b, α parameter space to determine the optimal energy. Since the atoms are spin-polarized, different χ -functions for different spin types were used. The QMC results, together with LDA results and experimental values, are presented in Table III. The approach gives carbon ionization energy and electron affinity in agreement with experiment within ± 0.2 eV (C^- is

Table III. The theoretical and experimental values of electron affinity and first ionization potential (in eV) for carbon. Statistic error in the last digits is in parentheses.

	E.A.	1st I.P.
LDA	C^- unbound	11.76
QMC	1.05(10)	11.43(5)
Experiment	1.27	11.26

Table IV. Terms in the total energy of diamond (64 electron simulation at a lattice constant $a = 3.63$ Å) for a single Slater determinant of LDA wavefunctions and for a Jastrow-Slater function with a two-body term only in the Jastrow factor, as discussed in the text, and with LDA wavefunctions in the determinant. Energies in eV/atom.

	Slater Det.	Jastrow-Slater (u only)
Local Pot.	-87.1	-73.6
Elec-Elec	-29.2	-39.0
Kinetic	121.3	116.8
Non-local Pot.	15.8	12.8
Ewald Sum	-171.0	-171.0
Total	-150.2	-154.0

unbounded in LDA). Since the number of three-body interactions is very different for the three cases, this result suggests that the three-body terms in the Jastrow factor can only lower the energy by no more than approximately 0.2 eV/atom.

The method has been applied to study the binding energy and structural properties of diamond. In the calculation, simulation cells containing up to 54 atoms (or 216 electrons) have been used. We find that the size dependence for larger simulations is almost entirely determined by the convergence of the single-particle terms in the total energy, as given within band theory by the k-point sampling of the Brillouin zone. The various contributions to the total energy for a specific simulation are given in Table IV illustrating the effects of electron correlation. As is shown in Table IV, the introduction of a Jastrow factor with only the two-particle term $u(r_{ij})$ lowers the total energy of the solid by approximately 3.8 eV/atom. With the introduction of the Jastrow factor, the electron-electron energy is substantially reduced. However, unlike uniform systems, the kinetic energy also decreases. It is the electron-ion (local plus nonlocal potential terms) which is greatly increased. The general trends in the atom are similar. Without the one-particle term χ in the Jastrow factor, the presence of a nonzero $u(r_{ij})$ alters the charge density from that of the Slater determinant alone. Because $u(r)$ is positive and a decreasing function of r , its effect is to remove charge from the high density regions leading to both an increase in the electron-ion energy and the decrease in the kinetic energy.

The total energies obtained with and without the full Jastrow factor (i.e., including both the u and χ terms) in the wavefunction are presented in Table V for diamond at the minimum-energy lattice constant together with the atomic results. The correlation energies for the valence electrons in the atom and the solid are thus found to be 2.4 ± 0.1 eV and 4.1 ± 0.2 eV/atom, respectively. These values are in agreement with results for the carbon valence electrons in a recent calculation using a similar ansatz for the many-body wavefunction but evaluating the energy by diagrammatic techniques.⁴⁴ Our value for the Hartree-Fock cohesive energy obtained using LDA wavefunctions in a single Slater determinant is 5.85 ± 0.25 eV/atom.

The final results for the binding energy of diamond in the present approach are also given in Table V and compared with the LDA result obtained using the Ceperley-Alder form for the exchange-correlation energy.⁴⁵ We

Table V. Total energies (in eV/atom) of the carbon atom and of diamond (with finite-size correction) for (a) LDA calculation, and for Monte Carlo calculations with (b) single Slater determinant of LDA wavefunctions and (c) Jastrow-Slater function with one- and two-body terms in the Jastrow factor. The expected statistical error in the last digits is in parentheses.

	Carbon Atom	Diamond	Cohesive Energy
(a) LDA	-146.79	-155.42	8.63
(b) Slater Det.	-145.55(7)	-151.3(2)	5.85(25)
(c) Jastrow-Slater	-147.93(3)	-155.38(6)	7.45(7)
(d) Experiment ^a	---	---	7.37

^asee Ref. 46.

have included the zero-point energy of the phonons in the energy for the solid. The quantum Monte Carlo calculation gives a cohesive energy of 7.45 ± 0.07 eV, as compared to the experimental value⁴⁶ of 7.37 eV/atom. This result is in significantly better agreement with experiment than the value of 8.63 eV/atom computed using the LDA formalism. To obtain the structural properties of diamond, the QMC total energies as a function of lattice constant are fitted with a Murnaghan equation of state, as shown in Fig. 6. We obtain a fitted equilibrium lattice constant of 3.54 ± 0.03 Å and bulk modulus of 420 ± 50 GPa, compared with experimental values of 3.567 Å and 443 GPa, respectively.⁴⁶

To assess further the accuracy of the method, we performed a calculation for graphite. We obtained a cohesive energy for graphite which is identical to the diamond cohesive energy within the statistical noise of 0.07 eV/atom. This result is in excellent agreement with experiment since experimentally, the binding energy of graphite is only 0.025 eV larger than that of diamond.⁴⁷

IV. SUMMARY AND CONCLUSIONS

We have discussed, in this brief overview, two new approaches for calculating the properties of materials going beyond density functional formalism. A self-energy approach for calculating the quasiparticle energies from first principles is presented. The electron self-energy operator is evaluated to first order in the dressed Green's function and the screened Coulomb interaction including local field effects. This method allows an ab initio determination of electronic excitation energies in crystals and at surfaces and interfaces which can be directly compared with spectroscopic measurements. Excellent results have been obtained for a wide-range of materials systems showing that the method is accurate and of predictive power. A method of calculating total energies of solids using nonlocal pseudopotentials in conjunction with the variational quantum Monte Carlo approach is also presented. Electron-electron correlation effects are treated using the exact interaction and a correlated Jastrow-Slater many-electron wavefunction. We demonstrated the computational feasibility of the method for solids and obtained the most accurate results to date for the cohesive properties of diamond and graphite. This development opens an exciting new theoretical avenue for studying the properties of solids, especially for the highly correlated electron systems.

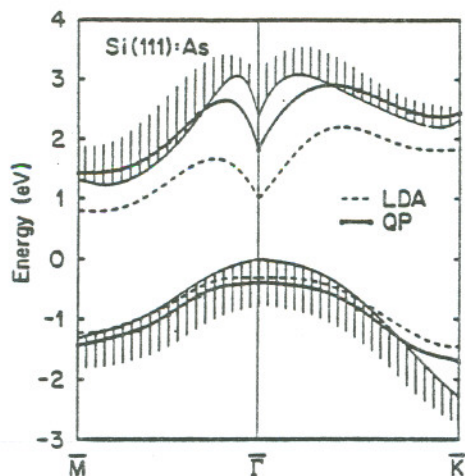


Fig. 3. Quasiparticle surface-state energies compared to LDA surface-state energies for the Si(111):As surface. Also shown is the quasiparticle bulk projected band structure.

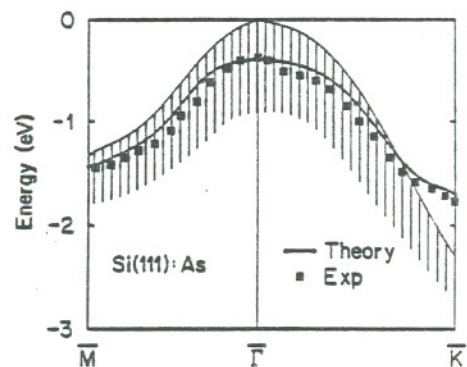


Fig. 4. Calculated filled quasiparticle surface-state energies for Si(111):As compared to data from photoemission (Ref. 31).

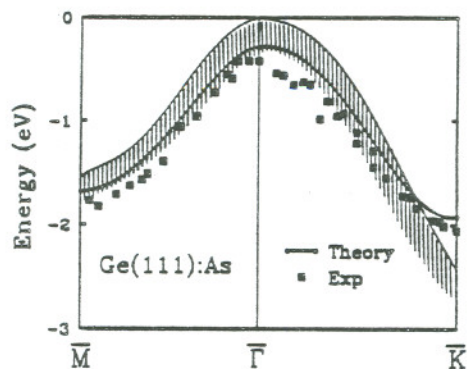


Fig. 5. Same as Fig. 4 except for Ge(111):As. Experiment data are from Ref. 32.

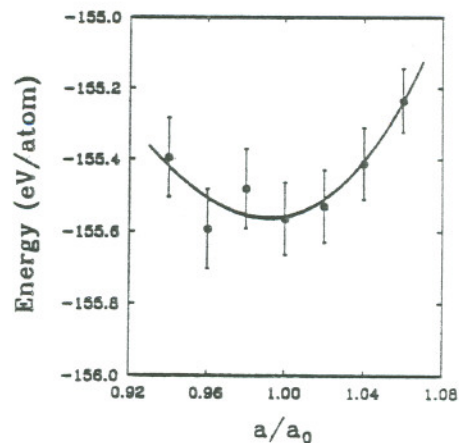


Fig. 6. Calculated total energy of diamond as a function of the ratio of the lattice constant to the measured lattice constant. The error bars indicate the standard deviation of the mean in each QMC calculation.

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